Photochemistry of cyclopentadienyliron(II) arene cations: analysis of the reaction with epoxides by means of time-resolved laser spectroscopy

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Abstract

We investigated the photochemistry of $(CpFeArH)^+ X^-$ in solutions containing epoxides by means of time-resolved laser spectroscopy. This study reveals that the key reactive intermediates are neutral complexes formed by the covalent attachment of the anion to the iron. The complex may be attacked by an epoxide and initiate a reaction sequence leading to crown ethers or to the polymerization of the epoxide. The reactivity of the neutral intermediates depends on the nature of the anion and the identity of the arene bound to the iron.

Introduction

The photoinitiation of cationic polymerization requires the development of light-dependent reactions that generate strong Brønsted or Lewis acids. Only a small number of such reactions with practical value are known. The most well-studied of these involve "onium" salts having anions of low nucleophilicity [1]. Direct or sensitized irradiation of diazonium, diaryliodonium, or triarylsulphonium hexafluorophosphate salts in epoxide-containing systems generate a Brønsted acid which can initiate polymerization or crosslinking.

Similarly, the irradiation of metal-containing photoinitiators may generate Lewis acids that can also cause polymerization or crosslinking of epoxides. Recently Meier and Zweifel [2] reported that certain iron arene salts $[(CpFeArH)^+ X^-$; Cp = cyclopentadienyl, ArH = aromatic hydrocarbon] are very effective photoinitiators for the polymerization of epoxides. These compounds are of special value because examples containing polynuclear aromatic hydrocarbons [ArH = pyrene (Pyr), for example] absorb light in the visible spectral region. Thus these iron arene salts are potentially capable of providing panchromatic sensitivity for epoxide-based photo-imaging systems.

The mechanism for the photodissociation of the arene from $(CpFeArH)^+ X^-$ complexes was investigated by Mann and co-workers [3]. They examined this reaction in nitrile-containing solutions and uncovered a key role for the triplet state

of the complex. We studied the reaction of the iron arene salts with nitriles by means of time-resolved absorption spectroscopy [4]. This work revealed a complex reaction pathway that depends on the state of association of the iron-arene cation with the anion. In non-polar solvents where the salt exists predominantly as ion-pairs, the initial reaction of the complex is with its associated anion to form a ring-slipped η^4-arene coordinatively saturated, but reactive, intermediate. In the rate-determining step of this reaction sequence, the iron-bound anion is displaced by a nucleophilic ligand (nitrile). In subsequent rapid steps the η^4-bound arene is replaced by two additional ligands to give the ultimate product, $(CpFe(L)_3)^+X^-$. This reaction pathway is outlined in eq. 1.
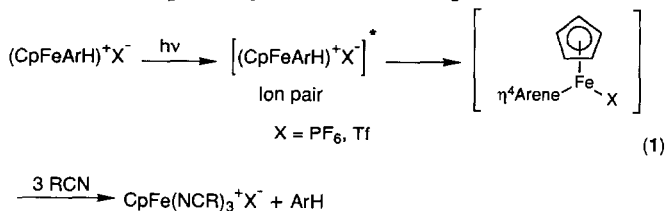
Meier and Rihs [5] studied the photochemistry of $(CpFeTol)^+PF_6^-$ (Tol is toluene) in dichloromethane solution containing an excess of ethylene oxide. They found that this reaction gives ferrocene and the bis-[12]crown-4 complex of iron(II). Later, Meier and Zweifel [2] examined the photochemistry of these iron arene salts in epoxide-containing films. From the results of these investigations it was suggested that the light-initiated reaction generates coordinatively unsaturated cyclopentadienyl iron. This species is proposed to be the Lewis acid that reacts to form a tris-epoxy-substituted iron-cyclopentadienyl cation [6]. Subsequent thermal reaction of this cation polymerizes the epoxide, eq. 2.
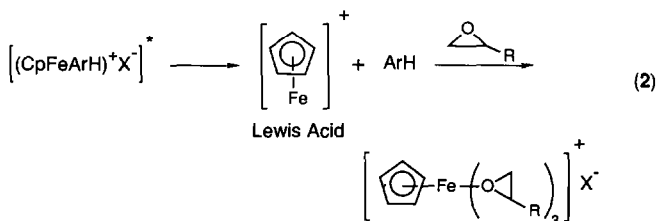
In this report we describe the time-resolved spectroscopic investigation of the reaction of photoexcited iron arene complexes with epoxides. Irradiation of (CpFe-Pyr)$^+$PF$_6^-$ in 1,2-dichloroethane (DCE) solution containing cyclohexene oxide (CHO) gives an anion-incorporated intermediate which subsequently reacts with CHO.

Results

Direct irradiation of a DCE solution of (CpFePyr)$^+$PF$_6^-$ (5×10^{-4} M) containing CHO (2.0 M) with visible light causes bleaching of the orange color of the iron complex without creation of a new absorption feature useful for the characterization of product formation. Similarly, irradiation of this solution with an excimer-pumped dye laser (386 nm, 10 mJ, 20 ns) does not generate a new absorbance that may be
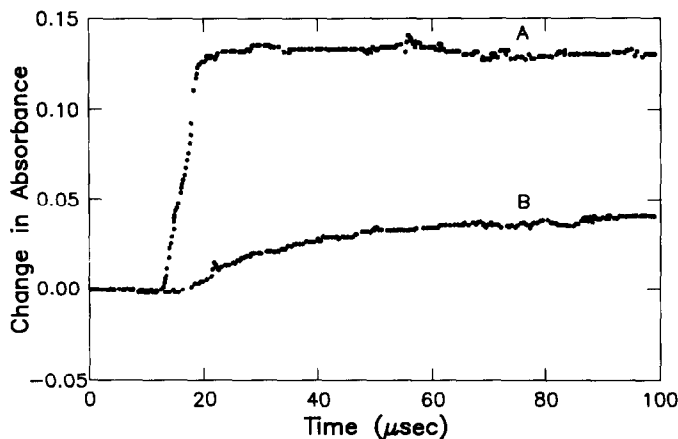
Fig. 1. Change in absorbance at 570 nm following laser excitation of $(CpFePyr)^+PF_6^-$: Curve A is observed in the presence of PhCN; curve B is obtained when both PhCN and CHO are present in solution.

assigned to an intermediate formed in the reaction sequence or to a stable product *. Thus we studied the reaction of CHO with photoexcited $(CpFePyr)^+PF_6^-$ in the presence of benzonitrile (PhCN) in order to visualize the reaction of the epoxide.

Irradiation of $(CpFePyr)^+PF_6^-$ in DCE containing PhCN (0.012 M) with the laser generates an absorption due to $(CpFe(NCPh)_3)^+$ ($\lambda_{max} = 550$ nm) that is formed in a kinetically first-order process with a rise time of 1000 ns. Under these conditions, the iron arene cation and its anionic counter ion exist predominantly as ion pairs in solution. Our previous investigation showed that photolysis of the ion pair gives the electrically neutral, counter ion-containing η^4-arene intermediate [4]. In the absence of CHO this intermediate reacts with PhCN to give, eventually, $(CpFe(NCPh)_3)^+$. When CHO is also present in the reaction solution, the anion-containing neutral intermediate may react with either PhCN or CHO.

Figure 1 shows the time dependence of the absorption change at 570 nm after laser irradiation of $(CpFePyr)^+PF_6^-$ in a PhCN-containing DCE solution in the presence and absence of CHO. It is apparent from inspection of this figure that the inclusion of CHO slows the formation of $(CpFe(NCPh)_3)^+$ and that the amount of this product formed in the presence of CHO is lower than in its absence.

To define more clearly the nature of the photogenerated intermediate that reacts with CHO, we studied the effect of counter ion structure on this reaction. Figure 2 is a plot of the ratio of the observed first-order rate constants for growth of the 570 nm-absorbing product in the presence of CHO (k_{obsd}) and its absence (k_0) against the CHO concentration. It is apparent that the presence of CHO has a much smaller effect on the reaction when Tf^- is the counter ion than when the counter ion is PF_6^-. This result indicates that the epoxide reacts with a counter ion-containing intermediate.

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* The CHO used in these experiments must be very carefully purified by fractional distillation. There is a trace impurity in reagent grade cyclohexene oxide that reacts with the excited state iron-arene complex to form an absorbing species: apparent $\lambda_{max} = 350$ nm.
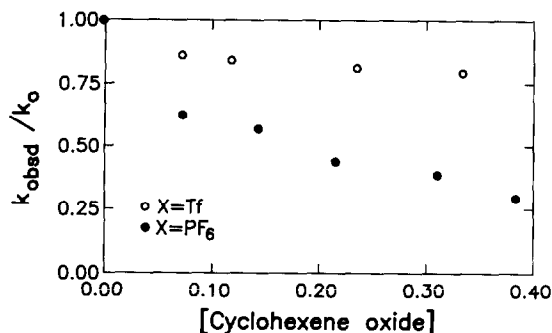
Fig. 2. Dependence of the rate constant ratio for reaction with CHO on the identity of the counter ion in $(CpFePyr)^+ X^-$.

The effect of the arene ligand on the reaction with CHO was probed by examining the difference in reactivity between $(CpFePyr)^+ PF_6^-$ and $(CpFeTol)^+ PF_6^-$. The data are shown in Fig. 3. The reaction of the toluene-containing complex with PhCN appears to be slightly more susceptible to inhibition with CHO than does the pyrene-containing complex. The differences are small — barely outside the
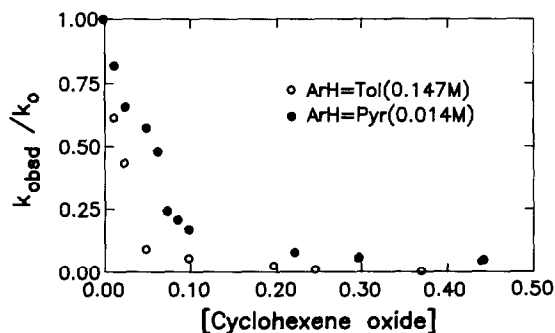

Fig. 3. Dependence of the rate constant ratio for reaction with CHO on the identity of the arene ligand in $(CpFeArH)^+ PF_6^-$.
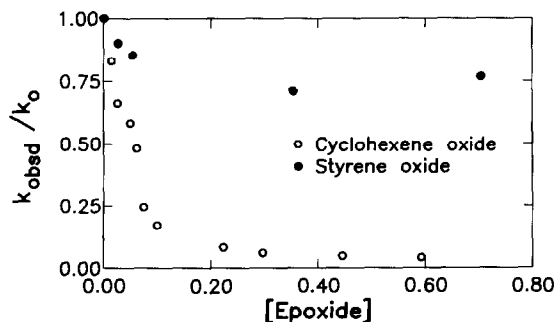

Fig. 4. Dependence of the rate constant ratio for reaction with epoxides with $(CpFePyr)^+ PF_6^-$.

experimental error at high CHO concentrations — but nevertheless indicate that the arene is attached to the iron in the intermediate that reacts with CHO.

Lastly, we examined the effect of the structure of the epoxide on the competition reaction with PhCN. The inhibitory effects of *cis*-2,3-epoxybutane and CHO are experimentally indistinguishable, but styrene oxide is a much less effective competitor than CHO. Figure 4 shows the rate of growth for the 570 nm-absorbing product in experiments containing identical concentrations of CHO and styrene oxide. The formation of product is slowed by CHO much more than by the styrene oxide, and the yield of $(CpFe(NCPh)_3)^+$ obtained with the former is lower than the latter.

Discussion

The results of these experiments support postulation of the reaction mechanism shown in Scheme 1. The processes shown in this scheme are consistent with the experimental observations. However, there must also be competing reverse reactions not shown in the scheme that affect the overall quantum yield. There are alternate mechanistic possibilities equally consistent with the available data.

Irradiation of the iron-arene complex paired with its counter ion gives the excited singlet state. There are four possible reaction paths available to this state that we cannot distinguish. The excited singlet state may react directly with its associated counter ion to give the anion-incorporated η^4-arene intermediate. This intermediate may also be formed by reaction of the anion with a ground-state coordinatively unsaturated η^4-arene formed from the singlet excited state. Alternatively the excited singlet state could intersystem cross to the triplet before it reacts. Both triplet sensitization [4] and direct irradiation into the singlet–triplet absorption band [3] initiates reaction of the iron-arene cations, but these observations do not eliminate a possible role for the excited singlet state. Once formed, the triplet state of the complex could either react directly with the anion, or it could give the ground state unsaturated η^4-arene before combining with the anion. The result is the same whichever path is operating. The photochemical reaction of $(CpFeArH)^+X^-$ gives the anion-incorporated η^4-arene intermediate. In contrast to the previous proposal
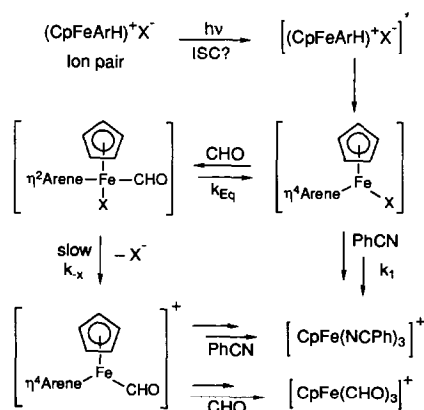
Scheme 1.

[6], we suggest that it is this intermediate which reacts with epoxides to begin the reaction sequence that leads to crown ethers or to polymerization.

In solutions containing both CHO and PhCN the anion-incorporated η^4-arene intermediate may react either with the epoxide or with the nitrile. The epoxide competes less effectively for this intermediate when Tf^- is the counter ion than when it is PF_6^-. This finding supports the proposed reaction mechanism. The more tightly bound triflate cannot be as easily displaced by epoxide as can the less nucleophilic hexafluorophosphate. The difference in reactivity between the Tf^- and PF_6^- containing intermediates is not as great when the attacking ligand is PhCN. This is consistent with commonly observed reactivity-selectivity principle. The more reactive intermediate (PF_6^--containing complex) is the less selective reactant.

The postulated reaction mechanism is also supported by the difference in reactivity between the toluene and pyrene containing intermediates. Pyrene is a better electron donor than is toluene and, therefore, the pyrene-containing intermediate should be less susceptible to attack by nucleophiles. The reactivity–selectivity principle again allows rationalization of the results. The more reactive toluene complex discriminates less effectively between PhCN and CHO than does the less reactive pyrene complex.

Additional details of the reaction mechanism are revealed by the findings that addition of CHO to a PhCN-containing solution of $(CpFeArH)^+X^-$ maintains first-order reaction kinetics and results in a decrease in the observed pseudo first-order rate constant (k_{obsd}). This rate constant depends on the identity of the counter ion even at extrapolated infinite CHO concentration. The mechanism outlined in Scheme 1 is the simplest proposal consistent with these observations. Kinetic analysis of the proposed mechanism reveals:

$$k_{obsd} = k_{-X} + k_1[PhCN]/(K_{Eq}[CHO])$$

where k_{-X} is the rate constant for loss of the counter ion from the η^2-arene intermediate, k_1 is the rate constant for reaction of η^4-arene anion-incorporated intermediate with PhCN, and K_{Eq} is the equilibrium constant shown in the scheme. We identify the loss of the counter ion from the η^2-arene intermediate as the rate-limiting step in the reaction sequence at high (infinite) CHO concentration. This reaction is likely to be slow since it generates charged products in a non-polar environment. It is also reasonable that this reaction is slower than its analogous step in the PhCN-containing intermediate since the nitrile is better able to stabilize the expected product. However it is clear that the results available do not permit certain identification of the reactive intermediate(s) involved in this reaction. For example, the exchange of ligand from epoxide to nitrile might occur exclusively from one intermediate or competitively from the mono-, bis-, or tris-epoxy-containing complexes.

In summary, investigation of the photochemistry of $(CpFeArH)^+X^-$ in solutions containing epoxides reveals that key reactive intermediates are neutral complexes formed by the covalent attachment of the anion to the iron. The reactivity of the intermediate depends on the nature of the anion and the identity of the arene.

Experimental

General. Melting points were determined on a Büchi melting point apparatus in open capillaries and are uncorrected. ^{1}H NMR spectra were recorded on a Varian
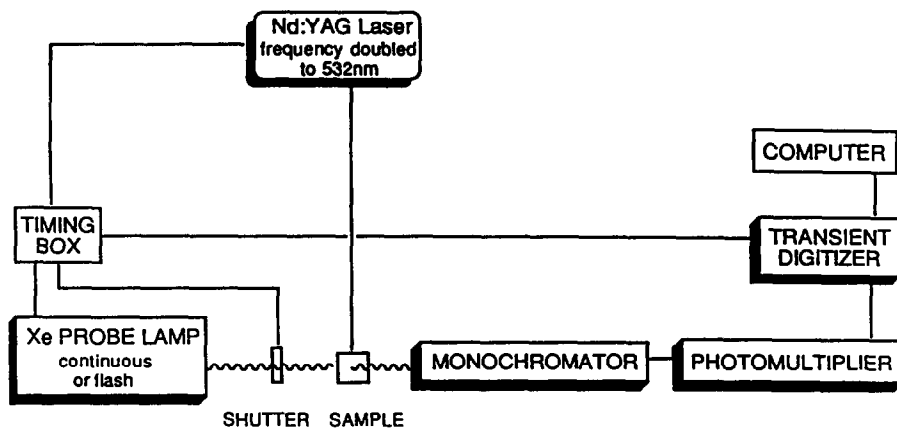
Fig. 5.

XL-200 or General Electric QE-300 spectrometer in $(CD_3)_2CO$ solution. UV-vis spectra were measured on a Perkin-Elmer 552 spectrometer. Elemental analyses were performed by the University of Illinois Microanalytical laboratory.

Benzonitrile was fractionally distilled under reduced pressure from CaH_2. Anhydrous 1,2-dichloroethane was stored with molecular sieves. Cyclohexene oxide (Aldrich Chemical Company) was distilled through a helix-packed Vigreaux column; only a middle cut was used.

Preparation of cyclopentadienyl iron(II)-arene complexes. The preparation of $[CpFe(ArH)]^+X^-$ proceeded as previously described [7]. The chloride salt formed in this procedure was exchanged for PF_6^- or Tf^- by treatment of an aqueous solution with HPF_6 or CF_3SO_3H. The solid products were purified by chromatography on neutral alumina eluting with CH_2Cl_2. The NMR spectral data were consistent with previous reports [4,7] and each compound gave satisfactory elemental analyses (C, H, Fe).

Laser spectroscopy. The laser spectroscopy was performed with a frequency doubled Nd-YAG laser and Xe probe lamp arranged perpendicularly: a schematic diagram of the apparatus is shown in Fig. 5. The laser power was kept below 20 mJ since we previously observed that higher power leads to transient species from the secondary irradiation of the first-formed products.

The concentration of the pyrene complex for the laser experiments was 0.014 M which gives an absorbance at 532 nm of 1.6 for a 1 cm path length. The concentration of the toluene complex was 0.15 M and the corresponding absorbance was 0.6. The samples were prepared in stopcock-equipped Pyrex cuvettes and were saturated with N_2 and protected from light before flash photolysis.

Acknowledgement

References

1 J.V. Crivello, ACS Symp. Ser., 242 (1984) 1; S.I. Schlesinger, Polym. Eng. Sci., 14 (1974) 513; J.V. Crivello and J.H.W. Lam, Macromolecules, 10 (1977) 1307.

2 K. Meier and H. Zweifel, J. Imaging Sci., 30 (1986) 174.
3 T.P. Gill and K.R. Mann, J. Organomet. Chem., 216 (1981) 65; T.P. Gill and K.R. Mann, Organometallics, 1 (1982) 485; T.P. Gill and K.R. Mann, Inorg. Chem., 22 (1983) 1986; J.L. Schrenck, M.C. Palazzoto and K.R. Mann, Inorg. Chem., 22 (1983) 4047; A.N. McNair, J.L. Schrenck and K.R. Mann, Inorg. Chem., 23 (1984) 2633; J.L. Schrenck and K.R. Mann, Inorg. Chem., 25 (1986) 1906.
4 D.R. Chrisope, K.M. Park and G.B. Schuster, J. Am. Chem. Soc., 111 (1989) 6195; D.R. Chrisope and G.B. Schuster, Organometallics, 8 (1989) 2737.
5 K. Meier and G. Rihs, Angew. Chem., Int. Ed. Engl., 24 (1985) 858.
6 A. Roloff, K. Meier and M. Riediker, Pure Appl. Chem., 58 (1986) 1267; L. Klingert, M. Riediker and A. Roloff, Comments Inorg. Chem., 7 (1988) 109.
7 A.N. Nesmeyanov, N.A. Vol'kerau and I.N. Bolesova, Tetrahedron Lett., (1963) 1725; C.C. Lee, K.J. Demchuck and R.G. Sutherland, Can. J. Chem., 57 (1979) 933; R.G. Sutherland, S.C. Chen, J. Pannekoek and C.C. Lee, J. Organomet. Chem., 101 (1975) 221.